Water-Quality Assessment of the Trinity River Basin, Texas— Nutrients and Pesticides in the Watersheds of Richland and Chambers Creeks, 1993–95

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Abstract

A study of nutrients and pesticides was conducted during February–August 1995 in the west-central part of the Trinity River Basin, where land commonly is used for growing crops. Water and bed-sediment samples were collected at 8 small reservoir sites in the headwaters (known as Natural Resources Conservation Service reservoirs), at 5 stream sites, and at 3 Richland-Chambers Reservoir sites. The analysis included data from the Chambers Creek near Rice site (08064100), which was sampled repeatedly during March 1993–September 1995.

Total nitrogen concentrations in the Natural Resources Conservation Service reservoirs were less than 1.0 milligram per liter, as nitrogen, except in 2 of the 8 reservoirs. For the five stream sites, total nitrogen concentrations at the beginning of the study ranged from 0.5 to 1.8 milligrams per liter. Peaks were noted in all stream sites during either March or April; the greatest peak concentration was 4.8 milligrams per liter, as nitrogen. By the end of the study, concentrations decreased to less than 1.2 milligrams per liter, as nitrogen. In the Richland-Chambers Reservoir, the February–March and June sampling showed total nitrogen concentrations of about 0.6 milligram per liter, as nitrogen.

At the beginning of the study, all five of the stream sites had total phosphorus concentrations less than 0.04 milligram per liter, as phosphorus. Peak concentrations in the streams occurred in the May sampling except at one site. Two sites had concentrations greater than 0.2 milligram per liter, as phosphorus. By the end of the study, concentrations decreased to less than 0.04 milligram per liter, as phosphorus, except at one site where the concentrations were about 0.08 milligram per liter. Concentrations in the Richland-Chambers Reservoir were less than 0.04 milligram per liter, as phosphorus.

Total nitrogen and total phosphorus concentrations generally increased with streamflow and with the percentage of cropland in the drainage area upstream from the sampling site.

Herbicides were detected in the streams much more often than insecticides were. Nineteen herbicides and 9 insecticides were detected at the 08064100 Chambers Creek near Rice site. Atrazine and metolachlor, the most commonly detected herbicides, occurred in all samples at this site. Other herbicides detected in 25 percent or more of the samples were alachlor, fluometuron, prometon, simazine, trifluralin, and 2,4-D.

At the beginning of the study, the number of herbicides detected in the five stream sites was 4 or 5. The greatest number of herbicides detected in the streams occurred in May samples, ranging from 7 to 10. The number of herbicides detected in the Richland-Chambers Reservoir ranged from 6 to 8. Generally, more herbicides were detected in high-streamflow samples than in low-streamflow samples. However, a consistent relation between the number of herbicides in samples and the percentage of cropland in a drainage area was not evident.

At the beginning of the study, atrazine concentrations at the stream sites were less than 0.4 microgram per liter, except at one site. In the streams, concentrations peaked in March and April; the greatest peak concentration was 20 micrograms per liter. By the end of the study, atrazine concentrations decreased to less than 0.4 microgram per liter at all the stream sites. In the Richland-Chambers Reservoir, the concentrations were about 1 microgram per liter during February–March and about 3 micrograms per liter in June. Atrazine concentrations tended to increase with increasing streamflow. A consistent relation between atrazine concentrations and the percentage of cropland in a drainage area was not evident.

The greatest number of insecticides detected in water samples was two. Diazinon, the most frequently detected insecticide, had slightly greater concentrations in May and June—between 0.01 and 0.02 microgram per liter.

The only organochlorine insecticides detected in bed-sediment samples from the watersheds were DDT and its metabolites DDD and DDE. All three compounds were detected in two Natural Resources Conservation Service reservoirs. The same two reservoirs are the only sites where DDD and DDT were detected. The greatest concentration of DDT was 6.3 micrograms per kilogram; DDD, 4.6 micrograms per kilogram; and DDE, 92 micrograms per kilogram.

INTRODUCTION

The U.S. Geological Survey (USGS) implemented the National Water-Quality Assessment (NAWQA) Program in 1990 (Leahy and others, 1990) with the following primary objectives:

- Describe the water-quality conditions of many of the Nation's streams and aquifers,
- Define long-term trends in water quality, and
- Identify, describe, and explain, to the extent possible, the major natural and human factors that affect water-quality conditions and trends.

NAWQA currently has 59 study units that provide building blocks of water-quality information across the Nation. Consistent plans and protocols allow information from the study areas to be aggregated and studied at the local, State, regional, and National levels. The strategy for implementing the program was to start about one-third of the study units in each of the fiscal years 1991, 1994, and 1997. The Trinity River Basin study in Texas (fig. 1) began in 1991.

NAWQA's approach to a water-quality assessment of streams is to (1) measure the physical properties and chemical constituents of water, (2) measure trace elements and organic contaminants in bed sediments and in organisms, and (3) characterize aquatic communities and habitat. This approach provides "multiple lines" of data to define and characterize water-quality conditions and to provide a baseline definition for determining changes and trends. All data are collected from networks of 8 to 12 sites within each study area. Some of the stream sites represent watersheds with rather uniform environmental settings; and others, generally on the mainstem of the river, represent complex parts of the

basin where there are a variety of point and nonpoint sources of contaminants and environmental settings. In watersheds that have numerous sources of contaminants, temporal variability is monitored by frequent sampling during seasons when contaminants such as fertilizers and pesticides are most available and storm runoff could transport them to the streams. In addition, occurrence and spatial variations of contaminants and hydrologic conditions during selected seasons are identified by synoptic surveys. Finally, temporal and spatial variability of contaminants in local areas are assessed by studies, such as the study documented in this report.

Water-quality issues in the Trinity River Basin were identified by a liaison committee comprising representatives from local, State, and Federal agencies and other agencies who have water-resources management responsibilities and expertise. Although basinwide contamination of streams by nutrients and pesticides has not been documented, nonpoint-source contamination in agricultural streams was identified as one of the major water-quality issues. To put this issue in perspective, the USGS conducted a study during February-August 1995 in the watersheds of Richland and Chambers Creeks (fig. 1). The watersheds are in a physiographic region of the Trinity River Basin where soils are fertile; an extensive farming economy has developed; and much of the runoff becomes drinking water for several municipalities in the Dallas-Fort Worth area. The study was part of an extensive data-collection program conducted in the Trinity River Basin during March 1993-September 1995 by the USGS (Land, 1995).

The primary purpose of this report is to improve the understanding of the occurrence and distribution of nonpoint-source nutrients and pesticides in streams draining an agricultural area with extensive cropland. More specifically, the purposes of this report are to show (1) nutrient and pesticide concentrations at several stream and reservoir sites and (2) how the concentrations and detections vary with time, with streamflow, with cropland, and with location in the watersheds. The scope of the report is limited to water and bed-sediment samples for nutrient and pesticide analyses collected during March 1993–September 1995 at sites in the watersheds of Richland and Chambers Creeks. The nutrients of concern are species of nitrogen and phosphorus, and the pesticides of concern are herbicides and insecticides in water and organochlorine insecticides in bed sediment.

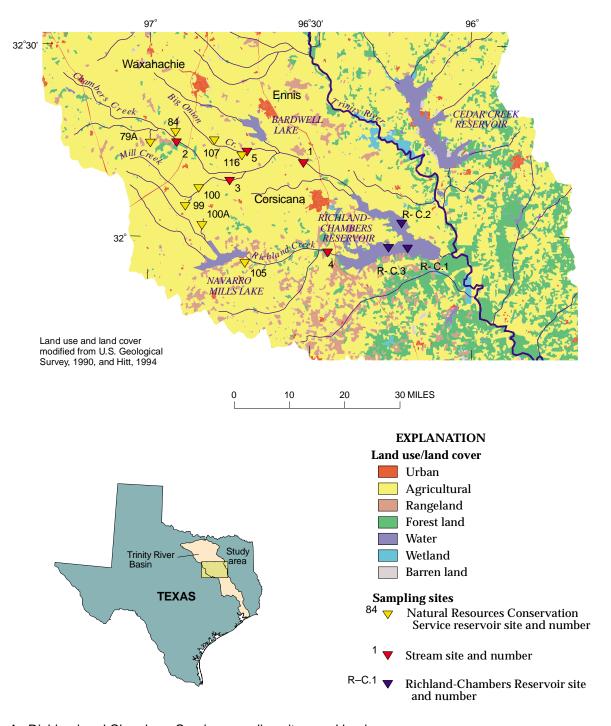


Figure 1. Richland and Chambers Creeks, sampling sites, and land use.

DESCRIPTION OF STUDY AREAS AND FERTILIZER AND PESTICIDE USES

The study area is in the west-central part of the Trinity River Basin and includes the watersheds of

Richland and Chambers Creeks and the Richland-Chambers Reservoir (fig. 1). The land use is primarily agricultural, consisting mostly of cropland and pasture with some rangeland. In cultivated areas, major crops are corn, cotton, sorghum, and hay. Some pecans and

oats also are grown. None of the crops are irrigated. In pasture and rangeland areas, cattle are the dominant livestock. Urban areas mostly are small rural communities supported by farming and ranching. Relatively large urban centers are Ennis, Waxahachie, and Corsicana.

The Richland-Chambers Reservoir captures all the streamflow from Richland and Chambers Creeks. It impounds about 1.2 million acre-ft of water at the conservation pool level. The reservoir is used mostly for municipal and industrial water supplies and for recreation. Upstream of the Richland-Chambers Reservoir, the larger reservoirs are Bardwell Lake in the Chambers Creek drainage area and Navarro Mills Lake on Richland Creek. They were built for flood control and water conservation. Each reservoir has a capacity slightly greater than 50,000 acre-ft at the conservation pool level. Finally, there are numerous flood-detention reservoirs with drainage areas of a few square miles or less constructed on private property by the Natural Resources Conservation Service (NRCS), formerly the Soil Conservation Service, of the U.S. Department of Agriculture. These reservoirs typically impound 200 to 1,000 acre-ft of water. Their outlet structures are designed to release increasing amounts of water as the stage rises above a conservation pool level. In all, about 25 percent of the drainage area upstream of the Richland-Chambers Reservoir is controlled by reservoirs.

Two major sources of nutrients in the streams are fertilizer from croplands and animal manure from cattle ranching. Other sources of nutrients include decomposition of organic matter, sewage effluent, atmospheric deposition, and dissolution of minerals, especially those containing phosphorus. Fertilizers are applied to crops from March to July, and applications vary with the crop, planting schedule, and weather. However, most of the applications are in May and June when plants are in the stage of vigorous growth. Some fertilizer is applied in the fall to pastures and fields where winter grass is grown for cattle. In urban areas, fertilizers are applied throughout the growing season, especially during March—May (Texas Agricultural Extension Service, written commun., 1995).

Herbicides, manmade chemicals to control or kill nuisance plants, often are used extensively in modern farming practices. The chemicals are applied to the soil in late winter or early spring before planting crops. Herbicides are applied again, as needed during the growing season, especially the early part. On the basis of esti-

mated pesticide use in the cropland area, atrazine is used on corn and, in combination with metolachlor, on corn and sorghum (Bill Harris, Texas Agricultural Extension Service, written commun., 1991). Metolachlor also is used independently on corn, cotton, and sorghum. Corn also can be treated with alachlor. Cotton is treated with several other herbicides, including fluometuron and trifluralin. Herbicides used on cotton, but not included in NAWOA laboratory analyses, are glyphosate, MSMA, and prometryn. Cotton also is treated with defoliants. Arsenic acid commonly was used for this purpose through 1994 but has been replaced primarily by paraquat. Herbicides such as 2,4-D and picloram are used in small amounts on hay fields but not at all on rangeland. Herbicides also are applied in urban areas. Residents, business owners, and municipal workers apply selective herbicides to kill weeds or prevent them from sprouting. Nonselective herbicides are applied to control all plants in limited areas along streets and highways, especially around signs, culverts, and bridges, and also in some landscape settings. According to a national survey of home pesticide use (Whitmore and others, 1992), herbicides commonly applied by homeowners include 2.4-D, acifluorfen, atrazine, dicamba, oryzalin, prometon, triclopyr, and trifluralin. Herbicides such as 2,4-D, dicamba, oryzalin, and simazine typically are used by municipalities.

Insecticides are used on corn and cotton in the area to control insects. These chemicals are applied in the late spring and early summer. The Texas Agricultural Extension Service estimates (Bill Harris, Texas Agricultural Extension Service, written commun., 1991) were used to identify commonly used insecticides for the area. Corn is treated with terbufos. Ethyl parathion is used on cotton, oats, and wheat; and methyl parathion is used on cotton and oats. Cotton also is treated with aldicarb, propargyte, and thiodicarb. Carbofuran is used on sorghum; dimethoate is used on pecans and wheat; and carbaryl is used on several minor crops such as hay, oats, pecans, and rye. In urban areas, insecticides are used most often to control insects in and near residences, businesses, golf courses, and parks. Many insect pests are a problem in spring when rain is more frequent and temperatures are moderate. However, other pests such as fire ants are a problem throughout the year. Insecticides are used extensively in the urban area for control of termites around buildings. Insecticides heavily used by homeowners include carbaryl, chlorpyrifos, diazinon, and malathion (Whitmore and others, 1992; and

Table 1. Location and description of sampling sites

Site no. (fig. 1)	U.S. Geological Survey station or identification no.	Location	Drainage area (square miles)	Percent of selected land uses in drainage area ¹			
				Cropland	Pasture and hay fields	Range- land	Urban and populated areas
		Natural Resources Conser	vation Serv	ice reservoir	s		
79A	321454096594801	Chambers Creek	2.2	0	0	93	4
84	321542096551201	Chambers Creek	6.0	55	40	0	4
99	320525096521601	Mill Creek	4.2	80	13	0	2
100	320737096503801	Mill Creek	7.8	60	35	0	1
100A	320124096500001	Richland Creek	4.3	85	15	0	0
105	315606096415401	Richland Creek	1.3	20	78	0	2
107	321436096475401	Big Onion Creek	1.9	82	16	0	0
116	321254096424801	Big Onion Creek	3.5	34	57	0	6
		Tributaries and ma	ainstem (str	eams)			
1	08064100	Chambers Creek near Rice	825	35	39	17	5
2	3214410096442601	Chambers Creek near Italy	346	32	28	33	4
3	321017096420099	Mill Creek	88	45	32	17	3
4	315801096282999	Richland Creek	718	29	56	8	2
5	321313096415201	Big Onion Creek	61	58	37	0	3
		Richland-Cham	bers Reserv	oir			
R-C.1	315800096083001	Confluence of Arms	1961	29	48	12	4
R-C.2	320629096221401	Chambers Creek Arm	961	35	41	16	5
R-C.3	315702096251601	Richland Creek Arm	735	29	57	9	2

¹ F.C. Baird, Natural Resources Conservation Service, written commun., 1996.

Mike Merchant, Texas Agricultural Extension Service, oral commun., 1996). Carbaryl, chlorpyrifos, and diazinon also are used by lawn-care companies and municipalities. Other commonly used insecticides not included in NAWQA laboratory analyses are acephate, pyrethrins, and pyrethroids such as permethrin, which is used on lawns and gardens and for termite control.

DATA COLLECTION

Water and bed-sediment samples for nutrient and pesticide analyses were collected at 8 small NRCS

reservoir sites in the headwaters, at 5 stream sites, and at 3 Richland-Chambers Reservoir sites (table 1). The five stream sites were sampled for nutrients and pesticides 7 times during the February–August 1995 study that focused on the watersheds of Richland and Chambers Creeks. The first and last samples provided data on the water-quality conditions at the beginning and end of the growing season. Because the intensive use of agricultural chemicals is early in the growing season, sampling was more frequent during this period. One of the 5 sites was 08064100 Chambers Creek near Rice, which was sampled repeatedly by the USGS

during March 1993–September 1995 to provide information on seasonal variations in streams draining agricultural areas. The eight NRCS reservoirs were sampled during July or August 1995. The data provided a composite sample of runoff during the spring and summer. The three Richland-Chambers Reservoir sites included the Chambers Creek Arm, the Richland Creek Arm, and near the confluence of the two submerged channels. These sites were each sampled twice—during February–March and in June 1995. Bed-sediment samples were collected once at each site. To summarize, all samples for data presented in this report were collected during February–August 1995, except for site 08064100 Chambers Creek near Rice where the data were collected during March 1993–September 1995.

Water samples were collected using compositedwidth and -depth field sampling techniques (Shelton, 1994). The samples were immediately processed and preserved to prevent contamination and constituent degradation. Finally, samples were taken to the field office or express mailed to the laboratory for preservation or immediate extraction of the constituents. The nutrient laboratory analysis provides dissolved ammonia, dissolved and total ammonia plus organic nitrogen, nitrite, nitrite plus nitrate, dissolved phosphorus, dissolved orthophosphate, and total phosphorus data. The pesticide laboratory analysis for water provides data for about 80 pesticides. The method detection limits for pesticides ranged from 0.004 to 0.05 µg/L (S.R. Glodt, USGS National Water Quality Laboratory, written commun., 1994). However, the laboratory analyst often provided a substantially lower concentration as an estimated value to be entered into the data base. Other laboratory analyses of water samples were for major inorganic ions, organic carbon, and suspended sediment. Field measurements of stream discharge, specific conductance, pH, water temperature, and dissolved oxygen also were made.

Quality-assurance and quality-control (QA/QC) procedures for water comprised submitting field blank samples (organic free water) and duplicate samples for analyses. The blank samples were sent to the laboratory to detect any contamination that would have occurred between the time of stream sampling and the final laboratory analyses. About 15 percent of all samples were QA/QC samples. Nutrients and pesticides were not detected in any of the field blank samples. A review of the duplicate-sample data indicates that the concentration of a constituent in a given sample is usually within 10 percent (often much less) of the concentration in the

duplicate sample except for samples having very low concentrations.

Bed-sediment samples were composited from numerous surficial subsamples of fine-grained material using field-sampling techniques described by Shelton and Capel (1994). The samples were wet-sieved in the field to produce a sample with particle sizes of 2.0 mm or less. The detection limits for pesticides ranged from 1.0 to 5.0 μ g/kg. Other laboratory analyses for bed-sediment samples comprised trace elements, semivolatile organic compounds, and grain-size distributions.

QA/QC procedures included submitting a duplicate sample for every 5 to 10 bed-sediment samples. The results of the QA/QC data for bed-sediment samples show that the concentration of a constituent in a given sample usually is within 10 percent of the concentration in the duplicate sample except for samples having very low concentrations.

NUTRIENTS

Nutrients in streams include several compounds of nitrogen and phosphorus that can be dissolved in water or attached to suspended sediment. Their concentrations are influenced by many environmental and human factors, such as precipitation, runoff, instream processes, soil types, proximity to sources, and land use. Water-quality standards for selected nutrients in drinking water are listed in table 2.

Concentrations of Nitrogen and Phosphorus

Boxplots are used to compare the distribution of concentrations of each of several dissolved and total (dissolved plus suspended) nitrogen and phosphorus compounds for March 1993-September 1995 data from 08064100 Chambers Creek near Rice (fig. 2). Total nitrogen concentrations range from 0.35 to 7.5 mg/L, and the median concentration is 0.9 mg/L. Dissolved ammonia concentrations are less than 0.09 mg/L as N. At the median concentration, about 60 percent of the nitrogen is in the form of dissolved nitrite plus nitrate and about 40 percent is in the form of total Kjeldahl nitrogen (total ammonia and organic nitrogen). Total phosphorus concentrations range from 0.01 to 0.2 mg/L, and the median concentration is 0.04 mg/L. Dissolved phosphorus concentrations are less than 0.01 mg/L in more than one-half the samples, and all concentrations are less than 0.07 mg/L.

The U.S. Environmental Protection Agency (USEPA) has established a maximum contaminant level

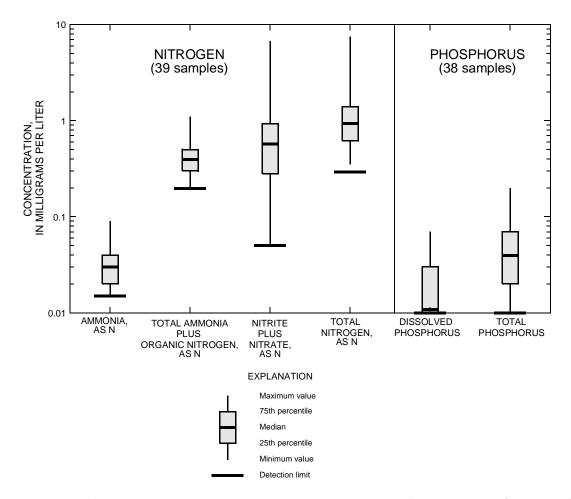


Figure 2. Distribution of nitrogen and phosphorus concentrations in samples from 08064100 Chambers Creek near Rice, March 1993–September 1995.

(MCL) for drinking water of 10 mg/L of nitrate as nitrogen (U.S. Environmental Protection Agency, 1996). To avoid excessive algae and other aquatic plant growth, USEPA recommends that total phosphorus be less than 0.1 mg/L in streams except where they enter lakes and reservoirs; there, the concentrations should be less than 0.05 mg/L (U.S. Environmental Protection Agency, 1986).

Relation to Seasons, Streamflow, and Cropland

Graphs of total nitrogen and total phosphorus concentrations for the March 1993–September 1995 data at 08064100 Chambers Creek near Rice illustrate seasonal variability (fig. 3). The peak concentrations of total nitrogen and total phosphorus are from samples collected during or immediately after a runoff event.

The graphs show total nitrogen concentrations tended to have short-term peaks from February to June and were highly variable from one year to the next. All samples with concentrations greater than 2.0 mg/L were collected during or immediately following runoff events, except for the sample collected in June 1994. Low concentrations (less than about 0.5 mg/L) occurred from July to September.

The data for total phosphorus indicate even more variability than the data for total nitrogen. Concentrations of total phosphorus greater than 0.1 mg/L occurred in January, February, May, and June. Also, these higher concentrations occurred in samples collected during or immediately following runoff events, except for the one collected in June 1994 (fig. 3). Concentrations of total phosphorus less than 0.05 mg/L were measured in every month except October.

Table 2. Water-quality standards for selected nutrient and pesticides in drinking water [MCL, maximum contaminant level; HA, health advisory; --, no standard has been established]

Constituent	U.S. Environmental Protection Agency MCL ¹	U.S. Environmental Protection Agency ${\rm HA}^2$			
	Nutrient (milligrams per liter)				
Nitrate	10 (as nitrogen)				
	Herbicides (micrograms per liter)				
Alachlor	2				
Atrazine	3	3			
Metolachlor		100			
Prometon		100			
Simazine	4				
Tebuthiuron		500			
2,4-D	70				
	Insecticides (micrograms per liter)				
Carbaryl		700			
Chlorpyrifos		20			
Diazinon		.6			

¹ U.S. Environmental Protection Agency, 1996.

Seasonally high concentrations of nitrogen appear to be related to the application of fertilizers to fields in the agricultural area and to lawns and land-scape plants in the urban area. However, the variability also is related to runoff events.

To explore the influence of streamflow on variability of total nitrogen and total phosphorus concentrations, graphs showing the relation of total nitrogen and total phosphorus to streamflow for 08064100 Chambers Creek near Rice are shown in figure 4. These graphs show a tendency for total nitrogen and total phosphorus concentrations to increase with streamflow. All samples with concentrations of total nitrogen greater than 2.0 mg/L, as nitrogen, and total phosphorus greater than 0.10 mg/L, as phosphorus, were collected when the discharge was greater than 100 ft³/s. During such periods, the daily mean discharge exceeded 100 ft³/s about 58 percent of the time.

To indicate the relation of nutrient concentrations to cropland, concentrations from data collected during

selected 1995 synoptic surveys of the stream sites and the NRCS reservoirs are graphed as a function of the percentage of cropland in the drainage area (fig. 5) of the sampling site (F.C. Baird, Natural Resources Conservation Service, written commun., 1996). Separating the concentration data by synoptic survey was necessary because of the large variability by season and by streamflow. The selected surveys were the first survey (February 23–March 2); the survey conducted when the concentrations generally were the greatest (March 15–17 for total nitrogen and May 9–11 for total phosphorus); and the last survey (July 31–August 17). Although there are exceptions, the concentrations of total nitrogen and total phosphorus tend to be greater when the percentage of cropland in the drainage area is greater.

Areal Variability

Areal variability of nutrients in the watersheds of Richland and Chambers Creeks is illustrated with

² Nowell and Resek. 1994.

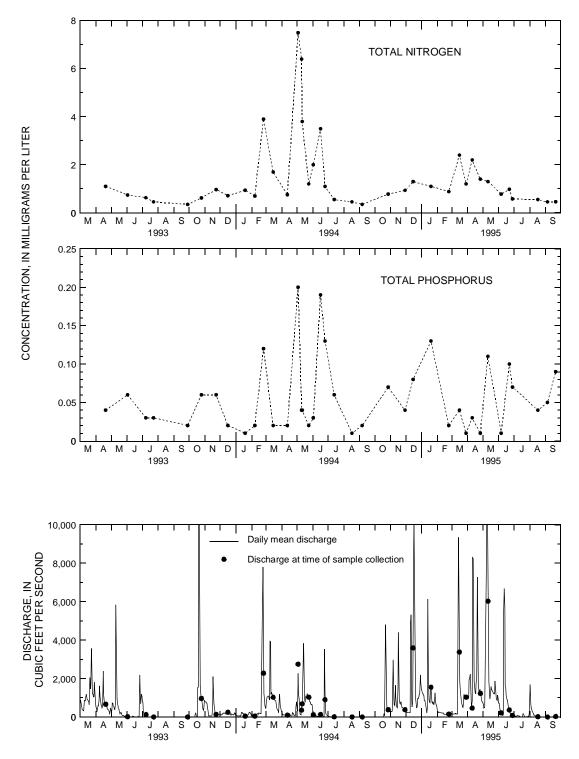


Figure 3. Seasonality of total nitrogen and total phosphorus concentrations in samples from 08064100 Chambers Creek near Rice, March 1993–September 1995.

graphs arranged schematically in the shape of the network of streams and reservoirs. Changes in nutrient concentrations can be noted as water moves through the headwaters area (represented by samples from NRCS reservoirs); through tributary and headwater streams; through the mainstems of Richland and Chambers

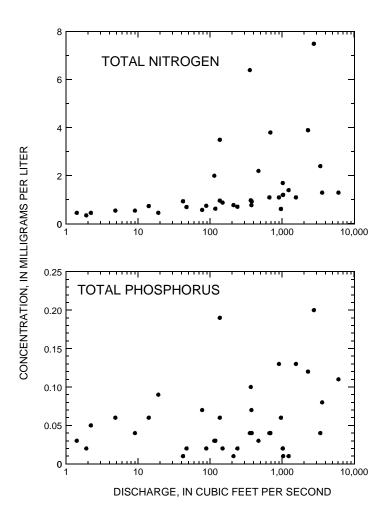


Figure 4. Total nitrogen and total phosphorus concentrations in samples in relation to streamflow, 08064100 Chambers Creek near Rice, March 1993–September 1995.

Creeks; and finally into the Richland-Chambers Reservoir.

The areal variability of total nitrogen is shown in figure 6. During the late July–August sampling of the NRCS reservoirs, the total nitrogen concentrations were less than 1.0 mg/L, as nitrogen, except for 1 reservoir in the Mill Creek drainage (No. 99) and 1 in the Richland Creek drainage (No. 105). Sampling of the NRCS reservoirs was interrupted at the very beginning by a major rainfall and runoff event. Sampling of reservoir Nos. 99 and 105 was done during the event; and the others were postponed for about 2 weeks. These differences in hydrologic conditions might be the reason for the exceptions.

For the five stream sites (tributary and mainstem) shown in figure 6, total nitrogen concentrations at the beginning of the sampling season ranged from 0.5 to 1.8

mg/L. Peak concentrations were noted in all stream sites during either March or April. The greatest concentrations occurred at Big Onion Creek and Mill Creek sites where the total nitrogen concentrations were between 4 and 5 mg/L, as nitrogen. By the end of the sampling season, total nitrogen concentrations at the stream sites were less than 1.2 mg/L, as nitrogen. For the three sample sites in the Richland-Chambers Reservoir, the February–March and June samples show that total nitrogen concentrations were about 0.6 mg/L, as nitrogen. Considering the June samples from this reservoir, the concentrations seem to be only a fraction of the average concentrations for the previous several months at the Richland Creek and Chambers Creek near Rice sites. This decrease in concentration indicates nutrients in the water are either being taken up by plants or settling to the bottom of the reservoir.

TOTAL NITROGEN

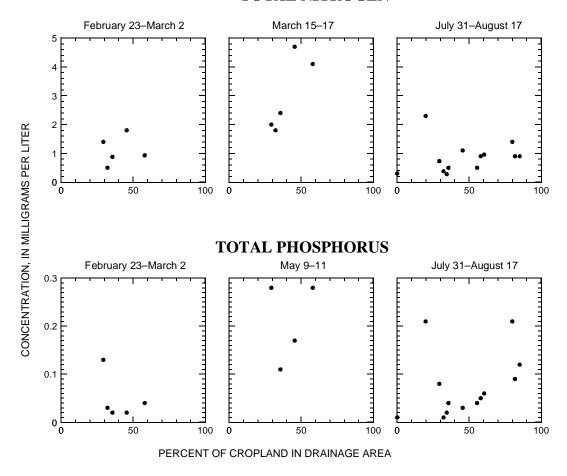


Figure 5. Total nitrogen and total phosphorus concentrations in samples in relation to percentage of cropland in drainage area for selected synoptic surveys in the watersheds of Richland and Chambers Creeks, February–August 1995.

The areal variability of total phosphorus is shown in figure 7. The NRCS reservoir sites had total phosphorus concentrations less than 0.12 mg/L, as phosphorus, except for 1 reservoir in the Mill Creek drainage (No. 99) and 1 in the Richland Creek drainage (No. 105). These NRCS reservoirs (Nos. 99 and 105) were noted previously as having higher total nitrogen concentrations possibly associated with rainfall and runoff during sampling. At the beginning of the sampling season, all the stream sites had total phosphorus concentrations less than 0.4 mg/L, as phosphorus. Peak concentrations occurred in May except for the site in the headwaters of Chambers Creek (near Italy). Only the Big Onion Creek and Richland Creek sites had concentrations greater than 0.2 mg/L, as phosphorus. By the end of the sampling season, all of the streams had concentrations less than 0.04 mg/L, as phosphorus, except for Richland Creek where the concentration was about 0.08 mg/L. Concentrations in the Richland-Chambers Reservoir were less than 0.04 mg/L, as phosphorus, during February–March and June.

PESTICIDES

Pesticides (herbicides and insecticides) in streams can include hundreds of synthetic compounds and their metabolites. These compounds can be dissolved in water or attached to sediment. The occurrence of pesticides in streams is related to application in the watershed and transport by runoff. Pesticide concentrations in streams and reservoirs are influenced by availability, transport, degradation, and instream processes. Water-

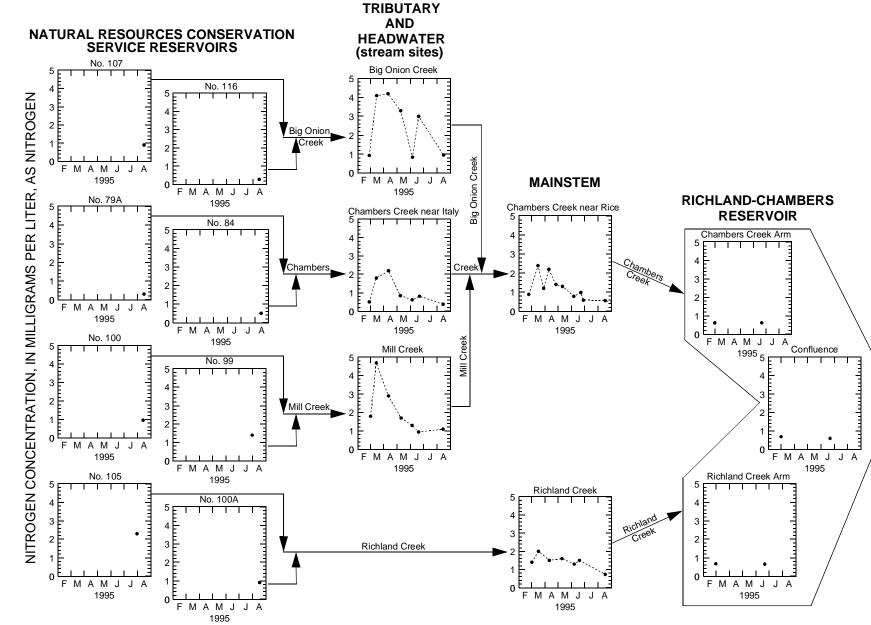


Figure 6. Total nitrogen concentrations in samples from the watersheds of Richland and Chambers Creeks, February–August 1995.

Figure 7. Total phosphorus concentrations in samples from the watersheds of Richland and Chambers Creeks, February–August 1995.

PESTICIDES

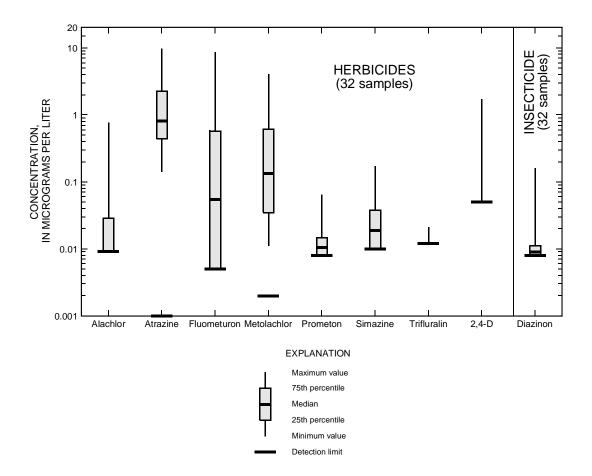


Figure 8. Distribution of selected herbicide and insecticide concentrations in samples from 08064100 Chambers Creek near Rice, March 1993–September 1995.

quality standards for selected pesticides in drinking water are listed in table 2.

Herbicides and Insecticides in Water

The water-sample analyses were studied to determine (1) the occurrence of herbicides and insecticides; (2) the variability with seasons in the number and concentrations of herbicides and insecticides in samples; and (3) the variability in concentrations of the herbicide atrazine with seasons, streamflow, percentage of cropland in the drainage area, and location in the watershed.

Detections and Concentrations

Herbicides were detected in the streams much more often than insecticides. Nineteen herbicides and 9 insecticides were detected at the 08064100 Chambers Creek near Rice site.

Boxplots of the concentrations of all the herbicides detected in 25 percent or more of the samples at

the 08064100 Chambers Creek near Rice site are shown in figure 8. Atrazine and metolachlor were detected in all the samples; atrazine concentrations are the highest, ranging from 0.15 to 10 µg/L. According to Texas Agricultural Extension Service estimates, atrazine and metolachlor are two of the most extensively applied herbicides in the agricultural area (Bill Harris, Texas Agricultural Extension Service, written commun., 1991). Atrazine is also in some products used for home lawn care. Atrazine and metolachlor also have been detected in air and rain samples in other studies, indicating the possibility of atmospheric deposition (Majewski and Capel, 1995). The cotton herbicide fluometuron was detected in about 75 percent of samples. Other herbicides detected in more than 25 percent of the samples were alachlor, prometon, simazine, trifluralin, and 2,4-D. The herbicides with concentrations greater than 1.0 µg/L are atrazine, fluometuron, metolachlor, and 2,4-D.

Atrazine is the only herbicide with concentrations greater than the applicable USEPA water-quality standard (Nowell and Resek, 1994). The USEPA health advisory (HA) for atrazine is 3 μ g/L; approximately 20 percent of the atrazine concentrations are greater than the HA (fig. 8).

Only one insecticide (diazinon) was detected in more than 25 percent of the samples (fig. 8). Diazinon was detected in about one-half the samples and also has the highest number of outdoor applications for insecticides according to the national survey of home pesticide use (Whitmore and others, 1992). Diazinon also is one of the most frequently used home insecticides in the Dallas-Fort Worth area (Mike Merchant, Texas Agricultural Extension Service, oral commun., 1996). Like atrazine and metolachlor, diazinon has been detected in air and rain samples in other studies (Majewski and Capel, 1995), indicating a possible atmospheric source.

None of the insecticide concentrations exceed the USEPA MCL or HA.

Relation to Seasons, Streamflow, and Cropland

Graphs showing the number of herbicides and insecticides detected in samples and the concentrations of atrazine and diazinon illustrate seasonal variability for March 1993–September 1995 at 08064100 Chambers Creek near Rice (fig. 9). Ten or more herbicides were detected in May and June samples. Five or more herbicides were detected in at least one sample from each month except February. More than six herbicides were detected in samples collected during or immediately following a runoff event. The greatest number of insecticides detected in any of the samples was two—in March, April, and May 1995. In all other months, the samples had one or no insecticides detected.

Atrazine concentrations tended to peak during April and May 1994 and during March and April 1995 at about 10 μ g/L (fig. 9). Relatively high concentrations began as early as February and lasted until as late as June, matching the seasonal application of herbicides to crops. Concentrations lower than 1.0 μ g/L prevailed from August to January. Atrazine concentrations following runoff events during February to June seemed to be influenced temporarily by runoff. If the runoff event was rather small, atrazine concentrations tended to increase; however, if the runoff event was very large, concentrations tended to temporarily decrease. Diazinon concentrations generally were higher during May and June; but are erratic because many of the samples

have no detectable concentrations or are just above the laboratory detection limit.

The relations of the number of herbicides in samples with streamflow and of atrazine concentrations in samples with streamflow are shown in figure 10 for the 08064100 Chambers Creek near Rice site. These graphs show that 5 or fewer herbicides were detected in samples throughout the range of streamflow; but when there are 6 or more herbicides detected in samples, the streamflow was always greater than $100 \ \text{ft}^3/\text{s}$. Atrazine concentrations tended to increase with increasing streamflow.

To determine the relation between the number of herbicides detected as well as atrazine concentrations in samples and the percentage of cropland in the drainage area, data from selected 1995 synoptic surveys of the 5 stream sites and the 8 NRCS reservoirs were graphed as a function of the percentage of cropland in the drainage area upstream of the sampling site (fig. 11). Separating the concentration data by synoptic survey was necessary because of the large variability by season and by streamflow between the sites. The selected surveys comprise (1) the first survey (February 23–March 2), (2) the surveys conducted when the detections and concentrations generally were the greatest (May 9-11, for number of herbicides detected in samples and March 15–17 for atrazine concentrations), and (3) the last survey (July 31-August 17). Considering the number of herbicides in samples, too few data points are in the first two surveys to identify a relation. For the July 31-August 17 survey, the number of herbicides detected does not seem to be related to the percentage of cropland in the drainage area. Atrazine concentrations decreased with percentage of cropland in the drainage area for the February 23-March 2 survey, increased for the March 15-17 survey, and were about the same for the July 31-August 17 survey; thus, no consistent pattern is evident.

Areal Variability

Areal variability of pesticides in the watersheds of Richland and Chambers Creeks is illustrated with graphs arranged schematically in the shape of the network of streams and reservoirs. Changes in the number of pesticides detected can be noted as water moves through the headwaters area (represented by samples from NRCS reservoirs), through tributary and headwater streams, through the mainstems of Richland and

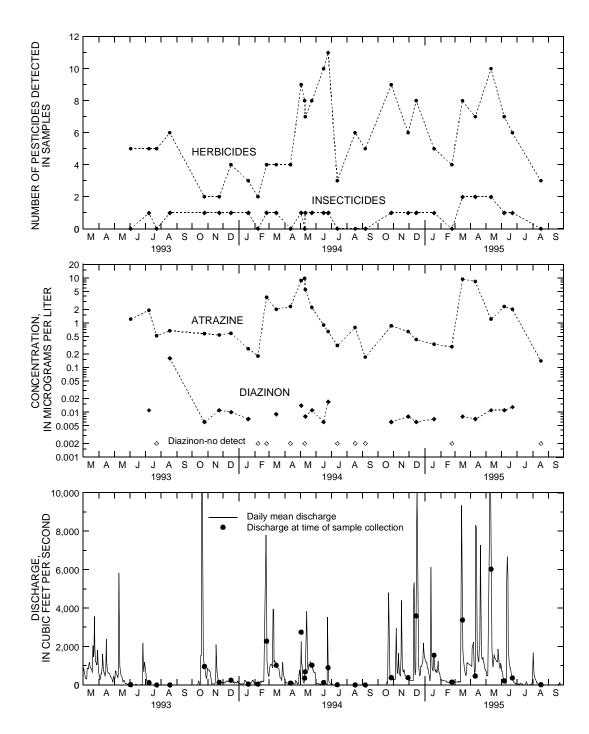


Figure 9. Seasonality of herbicide and insecticide detections of atrazine and diazinon concentrations in samples from 08064100 Chambers Creek near Rice, March 1993–September 1995.

Chambers Creeks; and finally into the Richland-Chambers Reservoir.

The areal variability of the number of herbicides in samples is shown in figure 12. End-of-season (July 31–August 17) sampling shows 3 or 4 herbicides in the

samples in the NRCS reservoirs. Two of the 3 tributary and headwater stream sites had 3 herbicides in the samples for the July 31–August 17 sampling period; Mill Creek had only 2 herbicides in the sample. At the beginning of the season, the number of herbicides in

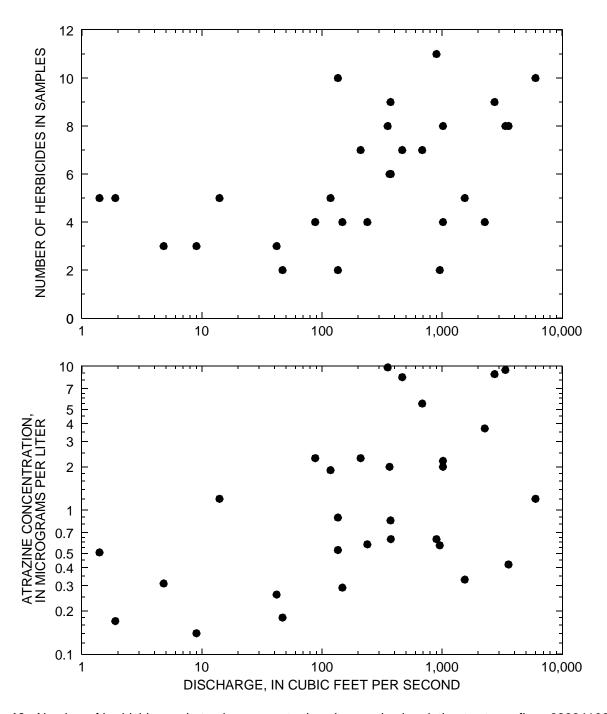


Figure 10. Number of herbicides and atrazine concentrations in samples in relation to streamflow, 08064100 Chambers Creek near Rice, March 1993–September 1995.

the stream sites was 4 or 5, not including Mill Creek, where the first sample is missing. The greatest number of herbicides in the stream sites was in the May samples, which ranged from 7 at the Richland Creek site to 10 at Chambers Creek near Rice site. The number of herbicides in the Richland-Chambers Reservoir ranged

from 6 to 8. The data indicate that the number of herbicides in the Richland-Chambers Reservoir tends to be cumulative of water coming from several sources.

The areal variability of atrazine concentrations is shown in figure 13. These graphs show that concentrations ranged from 0.05 μ g/L in NRCS No. 116 in

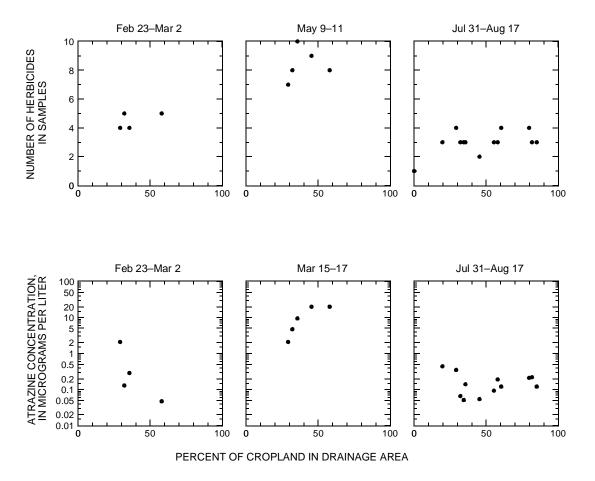


Figure 11. Number of herbicides and atrazine concentrations in samples in relation to percentage of cropland in drainage area for selected synoptic surveys in the watersheds of Richland and Chambers Creeks, February–August 1995.

the Big Onion Creek drainage, to 0.4 µg/L in NRCS No. 105 in the Richland Creek drainage. These samples were collected during July 31-August 17 when the concentrations were most likely to be low. At the beginning of the season, atrazine concentrations at the stream sites were less than 0.4 µg/L, except at Richland Creek where the concentration was 2.0 µg/L. The Mill Creek sample for February is missing. At these stream sites, the concentrations peaked in March and April, with the greatest peak concentration (20 µg/L) in samples from Big Onion Creek and Mill Creek. By the end of the season, atrazine concentrations were less than 0.4 µg/L at all the stream sites. For the three sites in the Richland-Chambers Reservoir, the concentrations were rather uniform during each synoptic survey, about 1 µg/L during February–March and about 3 µg/L in June.

Organochlorine Insecticides in Bed Sediment

The accumulation of organochlorine insecticides in streambed sediment is a common contamination issue. This type of insecticide is hydrophobic and persists in the environment despite its discontinued use.

The only organochlorine insecticides detected in bed-sediment samples from the watersheds were DDT and its metabolites DDD and DDE. The areal variability in the concentrations of these compounds is shown in figure 14. DDE is the most common of these compounds and was detected at all sites except 2 of the NRCS reservoirs, 1 stream site, and 1 Richland-Chambers Reservoir site. All three compounds were detected in the 2 headwater reservoirs in the Big Onion Creek drainage area; the same 2 NRCS reservoirs are the only sites where DDT and DDD were detected. The

Figure 12. Number of herbicides in samples from the watersheds of Richland and Chambers Creeks, February–August 1995.

PESTICIDES

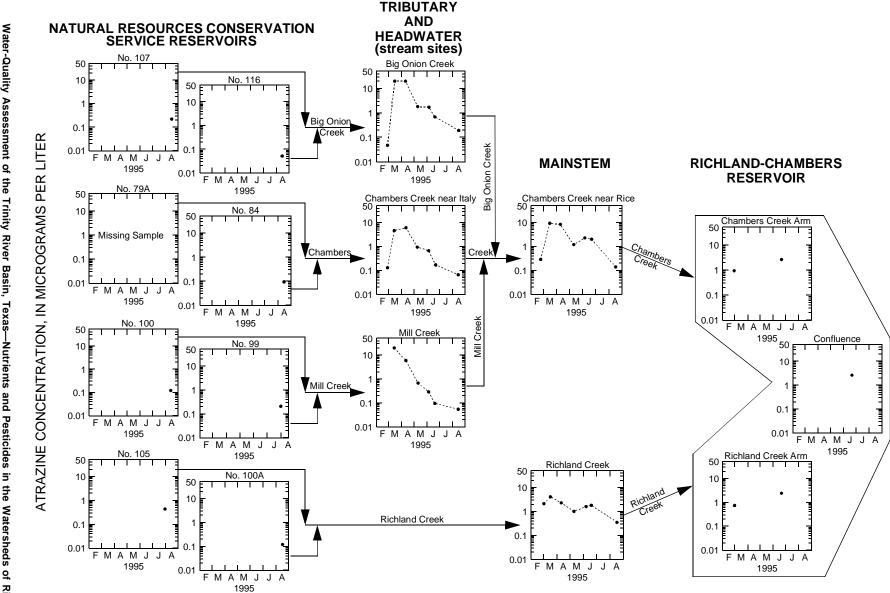


Figure 13. Atrazine concentrations in samples from the watersheds of Richland and Chambers Creeks, February-August 1995.

Figure 14. DDT, DDD, and DDE concentrations in bed-sediment samples from the watersheds of Richland and Chambers Creeks, February–August, 1995.

greatest concentrations of insecticides were in samples from NRCS No. 107; DDT was $6.3 \,\mu g/kg$, DDD was $4.6 \,\mu g/kg$, and DDE was $92 \,\mu g/kg$.

SUMMARY

A liaison committee for the Trinity River Basin NAWQA study identified nonpoint-source contamination in agricultural streams as one of the major waterquality issues. To put this issue in perspective, the USGS conducted a study of nutrients and pesticides in the watersheds of Richland and Chambers Creeks. The watersheds are in a physiographic region of the Trinity River Basin where soils are fertile; an extensive farming economy has developed; and much of the runoff eventually becomes drinking water for several municipalities in the Dallas-Fort Worth area.

Water and bed-sediment samples for nutrient and pesticide analyses were collected at 8 small reservoir sites in the headwaters (NRCS reservoirs), at 5 stream sites, and at 3 Richland-Chambers Reservoir sites during February–August 1995. The first and last samples provided data on the water-quality conditions at the beginning and end of the growing season. Sampling was more frequent early in the growing season. Bed-sediment samples were collected once during the 1995 study. The Chambers Creek near Rice site (08064100) was sampled repeatedly for nutrients and pesticides in water during March 1993–September 1995. Results of the nutrient analyses are summarized below:

- Total nitrogen concentrations ranged from 0.35 to 7.5 mg/L with a median concentration of 0.9 mg/L, and total phosphorus concentrations ranged from 0.01 to 0.2 mg/L with a median concentration of 0.04 mg/L at the 08064100 Chambers Creek near Rice site.
- Total nitrogen and total phosphorus concentrations tended to increase with streamflow.
- Total nitrogen and total phosphorus concentrations tended to increase with an increase in the percentage of cropland in the drainage area.
- Total nitrogen concentrations at the NRCS reservoirs were less than 1.0 mg/L, as nitrogen, except at 2 of the 8 reservoirs. For the five stream sites (tributary and mainstem), total nitrogen concentrations at the beginning of the study ranged from 0.5 to 1.8 mg/L. Peak concentrations were noted in all stream sites during either March or April; the greatest peak concentration was 4.8 mg/L, as

- nitrogen. By August, total nitrogen concentrations at the stream sites were less than 1.2 mg/L, as nitrogen. In the Richland-Chambers Reservoir, the February–March and June sampling showed total nitrogen concentrations of about 0.6 mg/L, as nitrogen.
- Total phosphorus concentrations in the NRCS reservoirs were less than 0.12 mg/L, as phosphorus, except at 2 of the 8 reservoirs. In February, all five of the stream sites had total phosphorus concentrations less than 0.04 mg/L, as phosphorus. Peak concentrations in the streams occurred in May except at one site. Two sites had concentrations greater than 0.2 mg/L, as phosphorus. By the end of August, all of the streams had concentrations less than 0.04 mg/L, as phosphorus, except one site where the concentration was about 0.08 mg/L. Concentrations in the Richland-Chambers Reservoir were less than 0.04 mg/L, as phosphorus.

Results of the herbicides and insecticides in water analvses are summarized below:

- Herbicides were detected in the streams much more often than insecticides were. Nineteen herbicides and 9 insecticides were detected at the 08064100 Chambers Creek near Rice site. Atrazine and metolachlor, the most commonly detected herbicides, occurred in all samples at this site. Other herbicides detected in 25 percent or more of the samples were alachlor, fluometuron, prometon, simazine, trifluralin, and 2,4-D. Atrazine concentrations tended to be the greatest, ranging from 0.15 to 10 µg/L.
- The greatest number of insecticides in samples was two. Diazinon, the most frequently detected insecticide, tended to have slightly greater concentrations in May and June, between 0.01 and 0.02 µg/L at the 08064100 Chambers Creek near Rice site.
- Five or fewer herbicides were detected in samples throughout the range of streamflow at 08064100 Chambers Creek near Rice site; but when 6 or more herbicides were detected in samples, the streamflow always was greater than 100 ft³/s. At the same site, atrazine concentrations tended to increase with increasing streamflow.

- A consistent relation between the percentage of cropland in a drainage area and the number of herbicides in samples was not evident. Atrazine concentrations decreased with decreased percentage of cropland for a survey at the beginning of the study, increased with increased percentage of cropland, and were about the same at the end of the study.
- The number of herbicides in samples from NRCS reservoirs was 3 or 4. At the beginning of the study, the number of herbicides in the five stream sites was 4 or 5. The greatest number of herbicides in the streams, ranging from 7 to 10, was detected in the May samples. The number of herbicides in the Richland-Chambers Reservoir ranged from 6 to 8.
- Atrazine concentrations in NRCS reservoirs ranged from 0.05 to 0.4 μg/L. At the beginning of the study, atrazine concentrations at the stream sites were less than 0.4 μg/L except at one site. In the streams, the concentrations peaked in March and April; the greatest peak concentration was 20 μg/L. By the end of the study, atrazine concentrations were less than 0.4 μg/L at all the stream sites. In the Richland-Chambers Reservoir, the concentrations were about 1 μg/L during February–March and about 3 μg/L in June.

Results of the organochlorine insecticides in bedsediment analyses are summarized below:

 The only organochlorine insecticides detected in bed-sediment samples from the watersheds were DDT and its metabolites DDD and DDE. All three compounds were detected in two NRCS reservoirs. The same two reservoirs are the only sites where DDT and DDD were detected. The greatest concentrations were: DDT, 6.3 μg/kg; DDD, 4.6 μg/kg; and DDE, 92 μg/kg.

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